

Surface Activity and Micellar Behavior of Dimethylamino- and Trimethylammonium- Tipped Oxyethylene–Oxybutylene Diblock Copolymers in Aqueous Media

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ABSTRACT: Surface activity and micellar behavior in aqueous media in the temperature range 20–50°C of the two block copolymers, $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$, ($\text{DE}_{40}\text{B}_{18}$) and $\text{I}^-\text{Me}_3\text{N}^+(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$, ($\text{TE}_{40}\text{B}_{18}$) in the premicellar and postmicellar regions have been studied by surface tensiometry, viscometry, and densitometry. Where E represents an oxyethylene unit while B an oxybutylene unit. Various fundamental parameters such as, surface excess concentrations (Γ_m), area per molecule (a_1^s) at air/water interface and standard Gibbs free energy for adsorption, ΔG_{ads}^0 have been investigated for the premicellar region at several temperatures. The thermodynamic parameters of micellization such as, critical micelle concentrations, CMC, enthalpy of micellization, ΔH_{mic}^0 , standard free energy of micellization ΔG_{mic}^0 , and

entropy of micellization ΔS_{mic}^0 have also been calculated from surface tension measurements. Dilute solution viscosities have been used to estimate the intrinsic viscosities, solute-solvent interaction parameter and hydration of micelle. Partial specific volume and density of the micelle were obtained from the density measurements at various temperatures. The effect of modifying the end group of the hydrophilic block was investigated by comparing the behavior of trimethylammonium- and dimethylamino-tipped copolymers, designated $\text{TE}_{40}\text{B}_{18}$, and $\text{DE}_{40}\text{B}_{18}$, respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3324–3332, 2010

Key words: block copolymers; adsorption; micellization; surface tension; density; viscosity

INTRODUCTION

Block copolymers of hydrophilic poly(oxyethylene) and hydrophobic poly(oxybutylene) in dilute aqueous solutions associate to form micelle, the hydrophobic block form micellar cores and are mainly responsible for the formation of micelles. The hydrophilic block forms the micelle corona and its length mainly determines the micellar size and interactions.^{1–4} The micellar and associative properties of block copolymers incorporating hydrophilic block of oxyethylene (E) units, $-\text{[CH}_2\text{CH}_2\text{O]}-$, and hydrophobic block of oxybutylene (B) units, $-\text{[CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O]}-$ in aqueous media have been studied in detail.^{1,5} To meet specific requirements for different applications, such as detergency, dispersion stabilization, foaming, emulsifications, and pharmaceutical applications, a number of internal parameters, such as molecular weight, chemical nature, block architectures, etc., and some external

parameters such as selection of solvent and conditions are adjusted.^{1,5,6} Among such parameters an important one is the nature of the end group, which may have significant effect on the micellar properties of diblock copolymers. For example, Kelarakis et al.⁷ have studied a range of E_mB_n copolymers ($m = 18$ – 184 , $n = 9$ – 18), and have reported that if the terminal hydroxy end of the B-block is methylated, the association number and thermodynamic radii are found to increase while the hydrodynamic radius is decreased. Maskos⁸ has also observed the effect of PEO-sided end group on the morphology and characteristic dimension of PEO–PBO polymeric particle in selective solvent. He noticed prominent changes in various properties for his end-group modified diblock copolymers. The effect of block composition, block length and block architecture on the micellar properties in aqueous media of block copoly(oxyalkylene)s in which hydrophilic poly(ethylene oxide) is combined with hydrophobic poly(propylene oxide), poly(1,2-butylene oxide) or poly(styrene oxide) have recently been reviewed.⁹ At a given temperature micellization of block copolymers can be achieved by increasing the concentration of block copolymers. The concentration at or above which the micellization start is called CMC (critical micelle concentration). CMC of block copolymers can be

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judged by many concentration dependent physical methods.¹⁰ Recently, Mansur and coworkers¹¹ have evaluated and compared the critical micelle concentration (CMC) for aqueous solutions of linear block copolymers, determined by using three different techniques: such as tensiometry, fluorescence, and light scattering, and the values of CMC found were in good agreements with each others. For the present work, we will use surface tension method, because the surface tension method is versatile as it can estimate not only CMC values but also provide vital information about adsorption characteristics of solutes at the air/water interface.¹⁰

The purpose of the work is to investigate the possible effects on the micelle properties by substituting the terminal part of the hydrophilic group by dimethylamino- and trimethylammonium-groups. The present work concerns on the micelle properties in aqueous solution of a trimethylammonium-tipped copolymer, $\Gamma\text{-Me}_3\text{N}^+(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$ (denoted $\text{TE}_{40}\text{B}_{18}$), and the dimethylamino-tipped, $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$ (denoted $\text{DE}_{40}\text{B}_{18}$). Under the experimental conditions, $\text{TE}_{40}\text{B}_{18}$ carries a charged tip, whilst the $\text{DE}_{40}\text{B}_{18}$ is apparently neutral.¹² As far as we are aware, there are no literature reports on the temperature dependence of CMC and other surface active properties for our copolymers. Moreover, we were interested to study micellar and surface activity at air/water interface using very basic, fundamental, and easily available techniques like surface tension, viscosity, and density.

EXPERIMENTAL

Preparation and characterization of copolymers

The block copolymers were synthesized by our research group at University of Manchester. The preparation of $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$ is described here from the previously published work.^{13,14} DAE, 2-dimethylaminoethanol (0.56 g, 6.28 mmol) was added by syringe to freshly distilled THF (25 cm³) in an ampoule under N₂. Potassium metal (ca. 0.09 g, 37 mol % DAE) was added piecewise to the stirred mixture over 10 min. The mixture was subjected to two freeze-pump-thaw cycles, and then stirred overnight at ambient temperature to allow all of the potassium to react, giving a clear solution. EO (16.73 g, 61.5 mol equivalent DAE) was transferred into the ampoule under vacuum. The temperature was gradually increased from ambient to 40°C over 13 days, after which time a thick, white precipitate was observed. A sample was removed for analysis. THF was transferred out of the ampoule and BO (13.55 g, 32.3 mol equivalent DAE) transferred in, under vacuum. The temperature was increased from 48 to 58°C over 7 days (yield 28.90 g). The average composition from nuclear magnetic resonance (NMR) end-group analy-

sis was $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{39}\text{B}_{18}$. The molar mass distribution of the copolymer was shown by gel permeation chromatography (GPC) to be narrow ($M/M_n = 1.06$). The trimethylammonium-tipped copolymer $\text{TE}_{40}\text{B}_{18}$ was formed by quaternization with iodomethane in methanol at ambient temperature in the dark. More detail for preparation and characterization of the copolymers have been fully described previously.^{13,14}

Surface tension measurements

Surface tension measurement was used for estimation of CMC and surface active parameters. The stock solutions (2 g dm⁻³) for each copolymer were prepared in deionized and doubled distilled water, and other copolymer solutions were obtained by diluting the stock solutions. The surface tension, (γ) of dilute aqueous copolymer solutions were measured at temperature in the range of 20–50°C, by detachment of platinum ring (4 cm circumference), using a torsion balance (White Elec. Inst. Co. Ltd., Model OS). The Torsion Balance (White Elec. Inst. Co. Ltd., Model OS) for surface tension measurement was supplied by Torsion Balance Supplies Co. (Warwickshire, England, United Kingdom). And the Stabinger Viscometer G2 (SVM 3000/G2) supplied by Anton Paar. The instrument was well protected from vibration and draught. A new solution was first equilibrated at lowest temperature for 1 h and then γ was measured after every 30 min until consistent readings were obtained. Thereafter, the temperature was raised, the solutions were re-equilibrated for 1 h, and the measurement procedure was repeated.¹⁵ Before using a new solution the ring was washed successively with dilute HCl and deionized water. To remove the possible effect of adsorption onto platinum ring, it was kept out of solution during temperature/concentration equilibration. Moreover to see the possible adsorption at the ring, each measurement was repeated three times with the same values of surface tension. Due to small surface area of the ring, however, no detectable adsorption was noticed, thus the change in surface tension was assigned to the adsorption of copolymers at air/water interface. The accuracy of instrument was checked by frequent determination of the surface tension of deionized water. The critical micelle concentration, CMC, were obtained from the plots of surface tension (γ) versus log C (where C is the concentration of the copolymers in g dm⁻³) in the aqueous solutions. The CMC was assigned to the concentration above which the surface tension remained constant.¹⁶

Viscosity and density measurements

Solutions of different concentrations for density and viscosity studies were prepared in deionized and doubled distilled water. Density and viscosity of

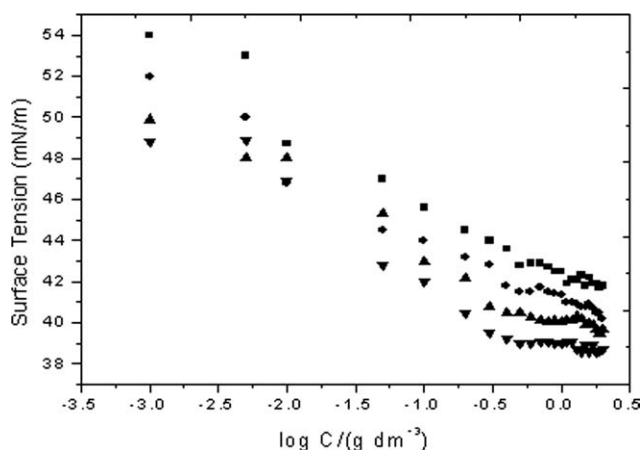


Figure 1 Typical plots of surface tension (γ) as a function of logarithmic of concentration ($\log C$) for aqueous solutions of $DE_{40}B_{18}$ at (■) 20°C, (●) 30°C, (▲) 40°C, and (▼) 50°C.

dilute aqueous solutions of block copolymers were measured in the temperature ranging from 20 to 50°C, with the help of Stabinger Viscometer G2 (SVM 3000/G2) supplied by Anton Paar. This viscometer combines the accuracy of conventional capillary viscometers with the speed and ease of use of Anton Paar's world-leading digital density meters. The instrument works in different measuring modes each having its own importance. We used M3 mode for our work, in which viscosity can be measured over wide temperature range (with intervals of 10°C) for a single solution. First the sample cell was cleaned and dried, and then sample (about 3 mL) was injected with the help of disposable syringe through the filling inlet and by pressing enter key of the instrument, it automatically starts measuring viscosity and density over the given range of temperatures. After 10 min, the results were displayed on the instrument screen and automatically printed with the help of a printer connected to the instrument. After each measurement, the sample cell was cleaned and dried with an air pump. To measure density and viscosity over a wide concentration range, we diluted the stock solution, and results were obtained by repeating the above procedure. The instrument directly gave the values of density, dynamic viscosity, and kinematics viscosity.

RESULTS AND DISCUSSIONS

Behavior of the hydrophilic end group

The two copolymers used in this work have the same block length and similar composition, the only difference occur at their hydrophilic end group. One has dimethylamino- group (denoted $DE_{40}B_{18}$), while the other posses trimethylammonium group (denoted $TE_{40}B_{18}$) at their modified ends. The possible local charge near the hydrophilic end and its effect on dif-

ferent parameters calculated for the two copolymers, we have to consider the nature of the end group. In the case of a trimethylammonium-tipped (T) copolymer, there is a positive charge and associated counterion, which contributes to a greater extent to excluded volume for the hydrophilic block, as compared to a purely nonionic polymer. Under the present experimental conditions, the solutions for dimethylamino-tipped (D) copolymer is expected and were found to be of neutral pH,¹² but this does not necessarily mean that the end groups are neutral, since there may be a different local pH in the immediate environment of the end group. Furthermore, because the amine is attached to an E chain, its local environment is effectively a mixed solvent of water and poly(ethylene glycol). For a low molar mass tertiary amine, such as triethylamine, the conjugate acid has a pK_a of about 11 at ambient temperature.¹⁷ If the D-tip had a pK_a of this magnitude, it can be calculated that there would be at least 80% degree of protonation under the conditions of the experiments. However, for tertiary amines incorporated into surfactants, pK_a values appear to be lower.¹⁸ On balance, we can expect that $DE_{40}B_{18}$ copolymers will partially be protonated under the conditions of the experiments. A protonated $DE_{40}B_{18}$ copolymer, like a $TE_{40}B_{18}$ copolymer, will carry a positive charge. However, a significant difference is that a DH^+ tip can form a hydrogen bond, either with an ether oxygen of the poly(ethylene glycol) block or with a nonprotonated D group. Thus intermolecular hydrogen bonding would stabilize micelle to a greater extent with higher aggregation number and size.¹²

Thermodynamic parameters of micellization and adsorption

Plots of surface tension (γ) versus logarithmic of copolymer concentration ($\log C$) for aqueous solutions of $DE_{40}B_{18}$ and $TE_{40}B_{18}$ in the temperature range 20–50°C, were plotted for determination of CMC. Only typical plots for $DE_{40}B_{18}$ at various temperatures are shown here in Figure 1. Following the previous practice,^{16,19,20} the CMC was assigned to the concentration at which the surface tension reached a steady value. Moreover, the CMC defines the point at which the complete Gibbs monolayer is formed and is used as an indirect indication of the concentration at which molecules first form associates in appreciable concentration, the arguments being that adsorption at the air/water interface is favored over micellization until full monolayer is formed. It may be noted that the effect is not itself indicative of the formation of large micelle, as it is possible for the surface tension curve to become constant when association is limited to dimers and not trimers.¹⁵ The values of CMC along with γ_{CMC} for both the copolymers are listed in Table I. It is clear

TABLE I
Critical Micelle Concentrations (CMC), Surface Tensions at CMC (γ_{CMC}), Free Energy of Micellization (ΔG_{mic}^0), Enthalpy (ΔH_{mic}^0), and Entropy of Micellization (ΔS_{mic}^0) for DE₃₉B₁₈ and TE₃₉B₁₈ in Aqueous Solutions at Different Temperatures

Polymer	T (°C)	CMC (g/L)	γ_{CMC} (mN/m)	ΔH_{mic}^0 (kJ/mol)	ΔS_{mic}^0 [kJ/(mol K)]	ΔG_{mic}^0 (KJ/mol)
DE ₃₉ B ₁₈	20	0.49	42.7	11.087	0.1012	-18.565
	30	0.45	41.51	11.100	0.1007	-19.413
	40	0.34	40.49	11.080	0.1018	-20.783
	50	0.29	39.22	11.072	0.1020	-21.874
TE ₃₉ B ₁₈	20	0.71	42.2	24.151	0.1427	-17.660
	30	0.66	41.3	24.151	0.1406	-18.450
	40	0.40	40.4	24.149	0.1422	-20.360
	50	0.30	39.1	24.130	0.1422	-21.800

Estimated uncertainties: $\pm 10\%$ in CMC; $\pm 4\%$ in γ_{CMC} ; $\pm 2\%$ in Γ_m ; $\pm 3\%$ in a_1^s ; $\pm 4\%$ in π_{CMC} ; $\pm 4\%$ in ΔG_{ads}^0 , ΔG_{mic}^0 , ΔH_{mic}^0 , and ΔS_{mic}^0 .

from the data that the values of CMC for DE₄₀B₁₈ are much lower than that of TE₄₀B₁₈, the effect is attributed to the difference in the end groups. The T-tipped copolymer has greater affinity for water as compared to D-tipped; hence the former copolymer needs more amount of its unimers to micellise. The CMC values for hydroxyl-ended group copolymers,¹ for examples for E₄₀B₈ and E₄₉B₁₈, are 0.33 and 0.30 g/L at 30°C, respectively. While some other diblock copolymers of the same class,⁹ E₉₆B₁₈ and E₁₈B₁₀ show these values 0.01 and 0.063 g/L as CMC. In our case, however, both the copolymers have the CMC values much higher than those in Refs. 1 and 9. This effect can be attributed to greater interactions/solubility of these copolymers with water due to dimethylamino- and trimethylammonium- groups at the hydrophilic ends. Our previous laser light scattering studies¹² on D/T-tipped modified copolymers and their comparisons with conventional E_mB_n copolymer showed prominent influence of end-group modification on various micellar parameters such as micelle size and aggregation number, etc.

The slope from the linear part of surface tension (γ) versus $\log C$ is related to the surface excess concentrations of the copolymer in the surface layer compared to the bulk, through Gibbs adsorption isotherm.^{10,19}

$$\Gamma_m = -\frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (1)$$

Within the assumptions that the concentration of solute in the solutions is negligible compared to that in the surface layer, by using the value of surface excess concentration (Γ_m), the area per molecule in the surface monolayer in square angstroms can be calculated from the relationship,

$$a_1^s = \frac{10^{16}}{N_A \Gamma_m} \quad (2)$$

where R is 8.314 J mol⁻¹ K⁻¹, T is absolute temperature in K, $\partial \gamma / \partial \log C$ is the slope of linear portions of the γ versus $\log C$ plots, N_A is the Avogadro's number and Γ_m is in mol cm⁻².^{10,19}

From the surface tension vs concentration profile we can also calculate surface excess pressure or surface pressure at critical concentration, π_{CMC} . Where $\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$, γ_0 and γ_{CMC} are the values of surface tension of pure water and of the solutions at CMC.^{16,21} The values of Γ_m , a_1^s and π_{CMC} are given in the Table II. It is clear from the table that for a given polymer the values of a_1^s increased with increase in temperature in the range 20–50°C. Soni et al.²² have also reported a similar increase in a_1^s values with increase in temperature for nonionic silicone surfactants. This increase in a_1^s could be due to the copolymers adsorbed at air/water interface with hydrophilic (-EO-) units probably oriented parallel to the surface, with one end anchored by the hydrophobic (-BO-) chain projecting outward from the surface, and the other end tending to move away from the surface into the bulk.²³ In our copolymers we have dimethylamino- and trimethyl ammonium groups at the end of hydrophilic -EO- block and it can be suggested that this dimethylamino- and trimethylammonium groups probably show preferential orientation toward the water surface because of hydration, the same explanation has been reported by Soni et al.²² for nonionic silicone surfactants. We can see that at a given temperature DE₄₀B₁₈ have higher values of a_1^s than TE₄₀B₁₈, means that the unimers of second copolymer have stronger interactions with water, and hence close arrangement. Relatively, a larger surface area was expected for T-tipped copolymer (cationic-tip) due to electrostatic repulsion among its unimers. But the opposite effect was observed in this case. Smaller area per molecule for this copolymer suggests stronger pull of water molecule in the bulk for the T-tipped hydrophilic portion of the copolymer. Thus, more stretching and

TABLE II
Surface Excess Concentrations (Γ_m), Area Per Copolymer Molecules (a_1^S), Surface Pressure (π_{CMC}), Free Energy of Adsorption (ΔG_{ads}^0), Enthalpy (ΔH_{ads}^0), and Entropy of Adsorption (ΔS_{ads}^0) for Dimethylamino- and Trimethylammonium-Tipped Oxyethylene-Oxybutylene Diblock Copolymers in Aqueous Solutions at Different Temperatures

Polymer	T (°C)	$\Gamma_m \times 10^{10}/\text{mol cm}^{-2}$	$a_1^S (\text{\AA}^2)$	π_{CMC} (mN/m)	ΔG_{ads}^0 (kJ/mol)	ΔH_{ads}^0 (kJ/mol)	ΔS_{ads}^0 [kJ/(mol K)]
DE ₃₉ B ₁₈	20	0.75	220	30.05	-58.742	376.06	1.083
	30	0.66	252	29.68	-64.504	392.65	1.083
	40	0.44	378	29.46	-87.890	426.90	1.083
	50	0.43	381	28.70	-87.054	436.90	1.083
TE ₃₉ B ₁₈	20	0.84	198	30.55	-54.160	277.80	0.763
	30	0.77	216	29.88	-57.306	288.50	0.763
	40	0.56	296	29.55	-73.033	311.85	0.763
	50	0.55	302	28.82	-74.345	321.00	0.763

Estimated uncertainties $\pm 3\%$ in Γ_m ; $\pm 4\%$ in a_1^S ; $\pm 3\%$ in π_{CMC} ; $\pm 5\%$ in ΔG_{ads}^0 , ΔH_{ads}^0 , and ΔS_{ads}^0 .

hence closer packing at the surface may be obtained due to stronger hydrogen bonding. While in case of D-tipped copolymer, less number of unimers are sufficient for surface coverage; hence, it shows more surface activity. Moreover, both these copolymers show higher surface activity and higher surface area per molecule as compared to conventional E_mB_ndiblock copolymers.²¹ The effect can further be attributed to the end-group modification.

For a closed association to micelles with narrow distribution of association number (N) the equilibrium between copolymers molecules (A) and micelles (A_N) can be written (concentration in mole dm⁻³). The association equilibrium can be written as,

$$A \rightleftharpoons [1/N] A_N$$

$$K_c = [A_N]_{\text{eq}}^{1/N} / [A]_{\text{eq}} \quad (3)$$

Hall in his detailed study showed that when association number N_w is very large, then the equation becomes,^{9,24}

$$K_c = 1/[A]_{\text{eq}}$$

$$K_c = 1/\text{CMC} \quad (4)$$

where $[A]_{\text{eq}}$ can be considered to be CMC. The standard Gibbs energy of micellization expressed per mole of chains may be calculated from the CMC as a molar concentration using the relationship.²⁴

$$\Delta G_{\text{mic}}^0 = -RT \ln K_c \quad (5)$$

$$\Delta G_{\text{mic}}^0 = RT \ln \text{CMC}$$

$$\Delta G_{\text{mic}}^0 = RT \ln (\text{CMC}/W) \quad (6)$$

R is gas constant, T is absolute temperature and W is the molarity of pure water.

The standard enthalpy of micellization is given approximately by;²⁴

$$\Delta H_{\text{mic}}^0 = \frac{-Rd[\ln K_c]}{d(1/T)} \quad (7)$$

As we cannot directly estimate K_c , so using eq. (4), K_c can be replaced by CMC: thus eq. (7) can be written as,

$$\Delta H_{\text{mic}}^0 = \frac{Rd[\ln \text{CMC}]}{d(1/T)} \quad (8)$$

The entropy of formation of micelles is given by,

$$\Delta S_{\text{mic}}^0 = (\Delta H_{\text{mic}}^0 - \Delta G_{\text{mic}}^0)/T \quad (9)$$

The standard enthalpy of micellization, i.e., ΔH_{mic}^0 was obtained from the slope of the plots of $\ln \text{CMC}$ versus inverse of temperature,¹² by using eq. (9) and Figure 2.

The standard Gibbs free energy of adsorption, ΔG_{ads}^0 in water for these copolymers can also be calculated from the standard Gibbs free energy of micellization using eq. (9) and the surface tension data using following equation.²⁵

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{mic}}^0 - \frac{\pi_{\text{CMC}}}{\Gamma_m} \quad (10)$$

where π_{CMC} is again the surface pressure at critical concentration and calculated as: $\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$, γ_0 and γ_{CMC} are the values surface tension of pure water and in the solutions at CMC. The standard Gibbs free energy for adsorption at air/water interface in the temperature range 20–50°C, was calculated by using the above eq. (10), and the values are listed in Table II. It is clear that all the values of ΔG_{ads}^0 are negative, indicating that the migration of

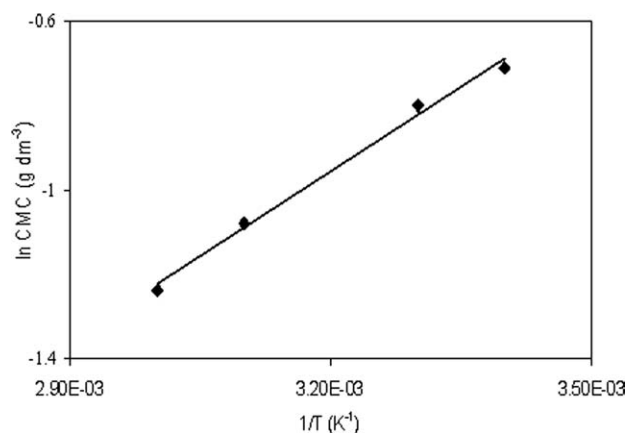


Figure 2 Logarithm of CMC versus inverse of temperature for aqueous solutions of DE₄₀B₁₈.

copolymers molecules in the monomer state to the air/water interface is a spontaneous process and favored by hydrophobic-hydrophilic balance (HHB) effect. At a given temperature, the higher value (more negative) values of ΔG_{ads}^0 for DE₄₀B₁₈ reflect more surface activity. It is also clear that for a given copolymer the value of ΔG_{ads}^0 becomes more negative with temperature, indicates rapid adsorption with temperature and hence early completion of Gibbs monolayer.

The calculated value of enthalpies of micellization, ΔH_{mic}^0 , for both copolymers are positive and this points to the well known fact that micellization is driven by positive entropy change associated with hydrophobic effect.^{25,26} This also shows that the micellization process is spontaneous but endothermic in nature. The very low ΔH_{mic} per B unit found for copolymers with the larger B blocks is attributable to those blocks being tightly coiled in the dispersed molecular state so that the interaction of B unit with water (hydrophobic interaction) is much reduced in comparison with the enthalpy of the units of short blocks, which are relatively extended in the molecular state. An unassociated copolymer with its hydrophobic block in such a tightly coiled state is often called a monomolecular micelle. Mejiro et al.²⁷ have reported that ΔH_{mic} decreases with increasing number of B units. Figure 3 shows the comparison of standard enthalpy of micellization per B unit of our tipped-copolymers with hydroxyl- and ethoxy-ended copolymers from earlier work.⁹ It can be seen that enthalpy per B unit decrease with increase in B-block length and hence with hydrophobicity. Both DE₄₀B₁₈ and TE₄₀B₁₈ follow the pattern shown by hydroxyl- and ethoxy ended copolymers with some deviation, which is due to the change in tipp. The lower value for DE₄₀B₁₈ reflects its more hydrophobic behavior as compared to TE₄₀B₁₈. In other words we can say that TE₄₀B₁₈ shows more

hydrophilicity and stronger interactions with water due to trimethylammonium group. This means that more bonds between E-chain and water have to be broken to form micelle.

The values of ΔG_{mic}^0 for each copolymer are negative and become more negative with increase in temperature which means that the rate of micellization increases with elevating temperature. At a given temperature the value of ΔG_{mic}^0 for DE₄₀B₁₈ is smaller than TE₄₀B₁₈; this can be attributed to more positive charge at the tip of the trimethylammonium-tipped copolymer. The effect of E-block length, on CMC and hence other thermodynamic parameters is not prominent. The change in entropy of micellization, ΔS_{mic}^0 for both copolymers is positive and nearly constant at all temperatures. The rapid increase in association number at higher temperature may make the micelle more compact and hence less freedom for B-block within the core of micelle.

During the process of micellization, the entropy change is always positive, it is because of two reasons: (i) structure of water molecules is affected and destroyed, as hydrophobic blocks are removed from the aqueous bulk to the interior of micelle at the interface and (ii) it also suggests that freedom of hydrophobic block in the interior of micelle is increased.¹⁰

The standard entropy of adsorption (ΔS_{ads}^0) was obtained from the slope of ΔG_{ads}^0 versus temperature (in Kelvin) plot, while the enthalpy (ΔH_{ads}^0) was deduced from the well known thermodynamic equation, i.e., $\Delta H_{\text{ads}}^0 = \Delta G_{\text{ads}}^0 + T\Delta S_{\text{ads}}^0$.^{10,25} The surface active and thermodynamic parameters are listed in Table II. The standard entropy of adsorption ΔS_{ads}^0 is positive; in all cases this reflects the greater freedom

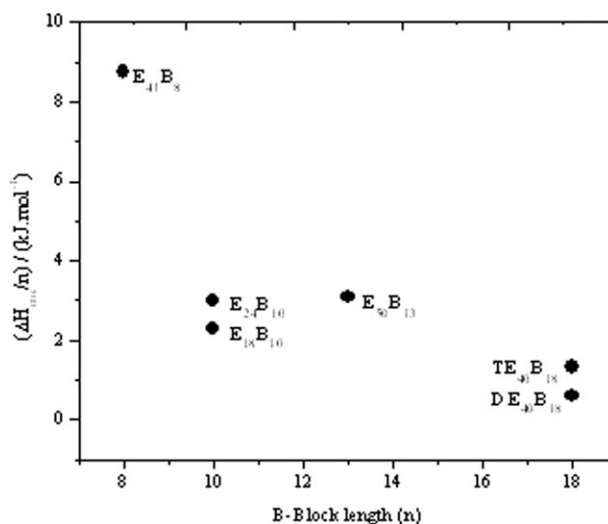


Figure 3 Standard enthalpy of micellization per B unit for aqueous solutions of hydroxyl-ended E_mB_n (for data see Ref. 9 and references therein), and values obtained for our tipped-copolymers, TE₄₀B₁₈ and DE₄₀B₁₈.

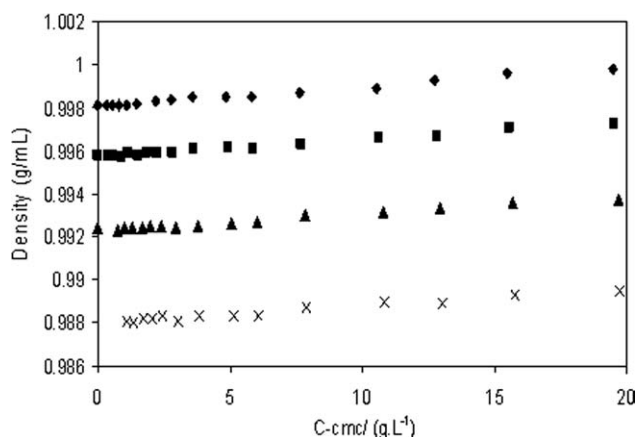


Figure 4 Plots of solution density versus C-CMC for aqueous solutions of DE₃₉B₁₈ at temperatures (◆) 20, (■) 30, (▲) 40, and (×) 50°C.

of copolymer molecule at air/water interface. The standard change in entropy of adsorption is greater than that of micellization for the same copolymer. This implies that there may be greater freedom of B-chain on the planner air/water interface as compared to the interior (core) of micelle. Moreover the dimethylamino-tipped copolymer has greater ΔS_{ads}^0 value as compared to the trimethylammonium-tipped copolymer, the effect can be attributed to more interactions of the latter's charged hydrophilic end with surface and hence hydrated monomers may be in more ordered form as compared to the first polymer. Likewise the enthalpy of adsorption ΔH_{ads}^0 is also positive in all cases which indicates the endothermic nature of adsorption process and become more endothermic at elevated temperature. As the ΔH_{mic}^0 values are less positive than the corresponding values of ΔH_{ads}^0 . This behavior shows that less number of bonds between E-chain oxygen and water are broken in micellization than in adsorption. The ΔH_{ads}^0 value for the dimethylamino-tipped co-

polymer is greater than the trimethylammonium-tipped, this again shows more adsorption for the second copolymer as compared to the first. The same is clear from surface excess concentration at air/water interface. From surface tension results, it is clear that the dimethylamino-tipped copolymer has lower adsorption but enhanced micellar properties than the trimethylammonium-tipped copolymer and this can be attributed to intermicellar charge effects. The possible local charge near the hydrophilic end and its effect on the copolymer solution is discussed in the start of discussion part.

Density and viscosity results

Density, intrinsic viscosity, and hydrations of micellar solutions

The partial specific volume of the micelles (\bar{v}_{mic}) was determined from the measured solution density (ρ_{soln}) values using relation as follow;²⁸

$$\rho_{\text{soln}} = \rho_{\text{solv}} + (1 + \bar{v}_{\text{mic}}\rho_{\text{solv}})(C - \text{CMC}) \quad (11)$$

Thus plotting (ρ_{soln}) versus C-CMC the intercept gives solvent density (ρ_{solv}) and from the slope the corresponding partial specific volume of the micelle (\bar{v}_{mic}) was obtained, the typical plots for DE₄₀B₁₈ are shown in Figure 4. By taking inverse of \bar{v}_{mic} , we got the micellar density (ρ_{mic}). The results are given in Table III. It is clear that the value of \bar{v}_{mic} show little increase with increase in temperature. This behavior is due to normal expansion hydrophobic block and thus the aggregation increase. As ρ_{mic} is inverse of \bar{v}_{mic} so the effect of temperature is also opposite for micellar density than micellar partial specific volume. At a given temperature, ρ_{mic} for TE₄₀B₁₈ is greater than DE₄₀B₁₈, this little difference could be attributed to the greater interactions of cationic charged-tipped with water. More water may be

TABLE III
Micellar Density, ρ_{mic} , Partial Specific Volume, \bar{v}_{mic} , Intrinsic Viscosity, $[\eta]$, and Interaction Parameter, K_H , for DE₄₀B₁₈ and TE₄₀B₁₈ in Aqueous Solutions at Different Temperatures

Polymer	T (°C)	ρ_{solv} (g/mL)	ρ_{mic} (g/mL)	\bar{v}_{mic} (mL/g)	$[\eta]$ (mL/g)	K_H (mL/g)
DE ₄₀ B ₁₈	20	0.9981	1.0970	0.9117	21.70	-23.04
	30	0.9957	1.0822	0.9240	17.40	-23.00
	40	0.9923	1.0787	0.9270	13.00	-23.00
	50	0.9880	1.0741	0.9310	14.00	-21.40
TE ₄₀ B ₁₈	20	0.9978	1.1086	0.9020	40.20	-14.92
	30	0.9962	1.0946	0.935	40.40	-17.32
	40	0.9925	1.0907	0.9168	40.90	-17.11
	50	0.9884	1.0743	0.9308	39.20	-15.30

Estimated uncertainties: $\pm 2\%$ in ρ_{mic} ; $\pm 3\%$ \bar{v}_{mic} ; $\pm 7\%$ in $[\eta]$; $\pm 9\%$ in K_H ; $\pm 8\%$ in.

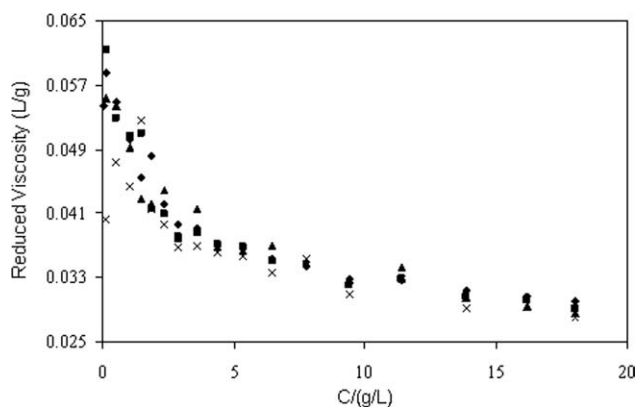


Figure 5 Typical plots of concentration dependence of reduced viscosity for aqueous solutions of TE₄₀B₁₈ at temperatures (◆) 20, (■) 30, (▲) 40, and (×) 50°C.

attached to its unimers/micelle and thus increase its overall mass.

Viscosity measurements provide very useful information on the hydrodynamic volume of micellar aggregates. The hydrodynamic volume is proportional to intrinsic viscosities, $[\eta]$, of micellar solutions.²² To obtain intrinsic viscosity, the dynamic viscosity (obtained directly from instrument) was converted to relative viscosity, η_r which was then converted to specific viscosity ($\eta_s = \eta_r - 1$) and finally to reduced viscosity. The intrinsic viscosity $[\eta]$ and intermicellar parameter (K_H) for each polymer at different temperature was obtained from the extrapolation of reduced viscosities to zero concentration following modified Huggins's relation as given below,²⁸

$$\eta_{sp/C-CMC} = [\eta] + K_H[\eta]C - CMC \quad (12)$$

Thus by plotting the graph of $\eta_{sp/C-CMC}$ versus $C-CMC$ as given in Figure 5, $[\eta]$ was obtained from intercept and K_H from the slope. When the solution concentration approaches zero, the intrinsic viscosity is defined by the following formula:²⁹

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp/C-CMC} = \lim_{c \rightarrow 0} \ln \eta_{r/C-CMC} \quad (13)$$

However for the whole concentration region Huggin's relation is not obeyed by the data. The dependence of reduced viscosities versus concentrations profiles in very dilute region (mostly in the concentration below 3 g dm⁻³) showed a nonlinear curvature and the values shoot up with the decrease in concentration for both the copolymers. Such deviation from the straight line is indicated by typical plots as in Figure 5. Soni et al.²¹ have also reported a similar complex dependence of reduced viscosities on concentration for diblock and triblock of poly-(oxethylene)-poly(oxybutylenes) copolymers. The

authors have reported that this trend occurs due to adsorption of the copolymers molecules on the capillary wall of viscometer, which in turn would increase the flow time and hence the measured η_{sp}/C values at low concentrations are apparent. These authors^{21,30} and especially Ohrn et al.³¹ have considered this effect to relate the true and apparent values of η_{sp}/C by,

$$(\eta_{sp}/C)^* = \eta_{sp}/C + \Delta \text{ and } \Delta \approx (\eta_r/C)(4a_{lay}/r) \quad (14)$$

where * indicates the apparent value. The terms a_{lay} and r in the Δ relation are the thickness of the adsorbed layer and the radius of the capillary of the viscometer used. In our case, we have used rotational viscometer which gives results in good agreement with capillary viscometer of capillary size, 0.300 mm. As for dilute solutions η_r close to unity, so η_{sp}/C values can be estimated by changing the chosen values for adsorbed layer thickness. In our case, the thickness of adsorbed layer was found to be nearly, 0.00022, 0.00026, 0.00030, and 0.00034 at 20, 30, 40, and 50°C, respectively for both the copolymers. This shows that adsorption effect increased with increase in temperature.

The values of intrinsic viscosities were obtained from the linear portion on the plots of reduced viscosities versus concentration, as shown in Figure 6. It is clear from Table III that the values of intrinsic viscosity for DE₄₀B₁₈ decrease with increase in temperature up to 40°C, which is a normal trend, but at 50°C there is a little increase in intrinsic viscosity this may be due to change in micellar shape at elevated temperature. For TE₄₀B₁₈, the values of intrinsic viscosity show a little increase with temperature but at 50°C there is a little decrease, again this may be due to change in shape, the change in viscosity value are not prominent for this copolymer with temperature as compared to DE₄₀B₁₈. At a given

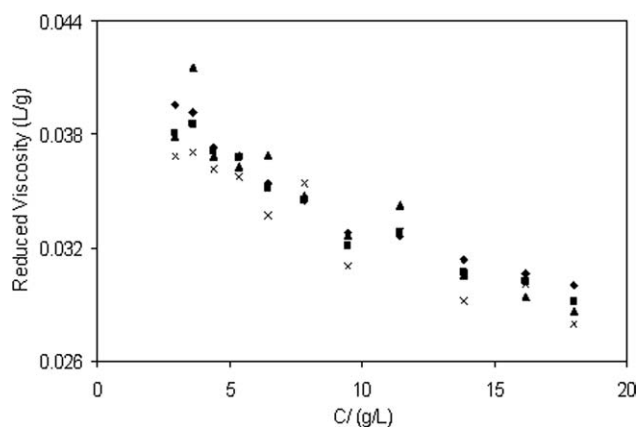


Figure 6 Typical plots of reduced versus C for aqueous solutions of TE₄₀B₁₈ at temperatures (◆) 20, (■) 30, (▲) 40, and (×) 50°C.

temperature, the values of intrinsic viscosity for $DE_{40}B_{18}$ are smaller than $TE_{40}B_{18}$; this is due to strong interaction with solvent due to charged-tipped, this is also supported by solvent-solute interaction (Huggin's parameter) parameter. Moreover, Kelarakis et al.³⁰ have also observed a prominent change in intrinsic viscosity with changing the hydrophilic end from hydroxyl to methoxy group. Their hydroxyl-ended copolymer ($E_{18}B_{10}H$) has a value of $3.8 \text{ cm}^3 \text{ g}^{-1}$ while that with methoxy-ended ($E_{18}B_{10}M$) got a value of $13.1 \text{ cm}^3 \text{ g}^{-1}$. The copolymer with smaller value was supposed to form spherical micelle while worm like micelle was assigned to the one ($E_{18}B_{10}M$) has higher intrinsic viscosities value. Similarly lower values (in the range of $3\text{--}6 \text{ cm}^3 \text{ g}^{-1}$) of intrinsic viscosities were reported for PEO/PBO diblock copolymers by Soni et al.²¹ In our case (see Table III), however, the very high values of intrinsic viscosities for both copolymers reflect the effect of end-group modification. These higher values point toward the formation of non-spherical aggregates under present experimental conditions.

CONCLUSIONS

Surface activity and micelle properties for aqueous solutions of both the copolymers, in the pre- and post-micellar-regions, are found to be temperature dependent. Both the adsorption and micellization process are spontaneous and endothermic in nature. Our results shows that both the copolymers tend to occupy more surface area at elevated temperature in the temperature range $20\text{--}50^\circ\text{C}$. The increase in the a_1^s with increase in temperature can be attributed to the orientation and hydration of dimethylamino- and trimethylammonium- groups at the tip of hydrophilic block. The effect of temperature was found to enhance the process of micellization and hence decrease CMC. The values of ΔG_{ads}^0 are more negative than ΔG_{mic}^0 and become more negative with increasing temperature in all cases, this show the more spontaneous nature of adsorption than micellization. $\Delta S_{\text{ads}}^0 > \Delta S_{\text{mic}}^0$, this reflects the greater freedom of B-chain at planner air/water interface as compared to the interior of micelle. We can conclude that both the adsorptions as well the micellization are entropy driven. Moreover D-tipped copolymer has enhanced micellar properties while T-tipped has greater surface activity. Viscosities and densities data also support the temperature dependent micellization/aggregation and change in the shape of aggregates with temperature. These higher values of intrinsic viscosities point toward the formation of non-spherical aggregates under present experimental conditions.

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